Supporting Information

Single Gold Trimers and 3D Superstructures

Exhibit a Polarization-Independent SERS Response

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The enhancement factors were determined by using the following expression:^[1]

 $EF = (I_{\text{SERS}}/N_{\text{SERS}})/(I_{\text{NRS}}/N_{\text{NRS}})$

- I_{SERS}: SERS intensity
- (integration time: 0.1 sec)
- N_{SERS} : number of molecules on the particle surfaces (100% adsorption) ($A_{\text{sphere}} = 4\pi r^2$; $A_{\text{molecule}}[2] = 0.26 \cdot 10^{-18} \text{ m}^2$) I_{NRS} : Raman intensity of the molecules in solution
- (integration time: 0.1 sec)
- N_{NRS}: number of molecules in solution $(V = 2\pi r^2 d; 2r = \lambda/(2N_A); d = 1 \text{ mm}; \lambda = 633 \text{ nm}; N_A = 0.7)$
- Dimer
 - \circ I_{SERS AVG} = 8.14 cts
 - \circ *I*_{SERS MAX} = 22 cts
 - \circ N_{SERS} = 96998
 - \circ $I_{\rm NRS} = 758$ cts in 30 sec
 - \circ N_{NRS} = 4.043 · 10¹²
- Trimer
 - \circ I_{SERS AVG} = 19.44 cts
 - \circ *I*_{SERS MAX} = 29 cts
 - \circ N_{SERS} = 130500
 - \circ $I_{\rm NRS} = 758$ cts in 30 sec
 - \circ $N_{\rm NRS} = 4.043 \cdot 10^{12}$
- Superstructure
 - \circ $I_{\text{SERS AVG}} = 13.33 \text{ cts}$
 - \circ *I*_{SERS MAX} = 20 cts
 - \circ N_{SFRS} = 77332
 - \circ $I_{\rm NRS} = 2069$ cts in 30 sec
 - \circ N_{NRS} = 9.829 · 10¹²



Figure 1S. A) SERS spectrum and B) LSPR spectrum of the Au/Ag superstructures in colloidal suspension. C) TEM image of a single Ag/Au superstructure.



Figure 2S: A) LSPR scattering spectrum of a single Au/Ag superstructure (raw data smoothed by a Savitzky-Golay filter). The LSPR measurements were performed with a modified WiTec Alpha 300 R microscope, a Zeiss 50x objective (bright- and dark-field, NA = 0.7) and a grating monochromator (30 cm focal length, 600 grooves/mm grating) equipped with a CCD (Andor iDus DU-401A BR-DD). For LSPR measurement the dark-field set-up was optimized using a halogen light source (Zeiss HAL100) and removing some optical parts (heat protection filter, AFM mirror, dichroic mirror). The raw LSPR spectra were corrected via Matlab by adding the spectral characteristics of the light source and by removing the scattered light from silicon wafer (substrate). B) SEM image of the single Au/Ag superstructure.



Figure 3S: Laser output power (632.8 nm line, HeNe) at the sample, with polarization filter (black line) and without polarization filter (blue dashed line). The polarization was rotated through 360° (10° intervals).



Figure 4S: TEM images of single Au dimers (30 nm gold spheres). Left: First gap size measurement. Right: Second time gap size measurement after few seconds. The gold spheres grew into each other due to the electron irradiation. Scale bar: 5 nm. The TEM measurements were performed with a transmission electron microscope (JEOL JEM 2100 with a LaB 6 cathode at 200 keV). The particles were deposited on C-coated Cu grids.



Figure 5S: A) – C): SEM images of single Au trimers and D) their corresponding single-particle SERS polarization dependence (A-C: solid black, dashed blue and dash-dotted red line). Laser output power: 5 mW. Integration time: 100 msec. Scale bar: 200 nm.



Figure 6S: Nanoparticle systems and their hot spots with one (monomer), two (dimer) and three nanoparticles (trimer). The black lines show the longitudinal modes.



Figure 7S: A) – C): SEM images of single Au/Ag superstructures and D) their corresponding single-particle SERS polarization dependence (A-C: solid black, dashed blue and dash-dotted red line). Laser output power: 5 mW. Integration time: 100 msec. Scale bar: 200 nm.



Figure 8S: Raman signal from the silicon wafer. Laser wavelength: 632.8 nm. Laser output power: 5 mW. Integration time: 100 msec. Maximum intensity: 368 cts. Minimal intensity: 242 cts. Average intensity: 300 cts. The polarization was rotated through 360° (10° intervals).